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Description

The present invention relates to a plastic lens having a high-refractive index and Abbe's number, and a method for the preparation of such lenses.

In recent years, plastic lenses are rapidly being more frequently utilized as optical elements in eyeglasses, cameras and the like, because they are lighter, more unbreakable and more dyeable than inorganic lenses.

A resin which can be prepared by the radical polymerization of diethylene glycol bis(allyl carbonate) (hereinafter referred to simply as DAC) has been used to prepare such lenses. This resin has a high impact resistance, is lightweight, and exhibits excellent dyeing properties and good workability of cutting and polishing.

However, lenses prepared from the above-mentioned resin have a lower refractive index ($n_D = 1.50$) than inorganic lenses ($n_D = 1.52$). In order to obtain equivalent optical properties to glass lenses, it is necessary to increase the central thickness, peripheral thickness and curvature of the lens and hence the lens becomes very thick. For this reason, resins having a high-refractive index are desired. Resins which have been previously used to prepare lenses having a high-refractive index include resins prepared by reacting an isocyanate compound with diethylene glycol (U.S. Patent No. 4,443,588), reacting an isocyanate compound with a hydroxyl compound containing a halogen atom such as tetrabromobisphenol A (Japanese Patent Laid-open Publication No. 164615/1983), or reacting an isocyanate compound with a hydroxyl compound containing a diphenyl sulfide skeleton (Japanese Patent Laid-open Publication No. 194401/1985).

The present inventors have previously proposed high-refractive plastic lenses comprising polyurethane resins or the like which can be prepared by reacting an isocyanate compound with a hydroxyl compound having a sulfur atom (U.S. Patent Nos. 4,680,369 and 4,780,552) or reacting an isocyanate compound with a polythiol (U.S. Patent No. 4,689,387 and Japanese Patent Laid-open Publication No. 267316/1987). DE-AS-1,045,641 relates to producing rubber-elastic bodies from components that include polyisocyanates and polythiols as well as acidic filling materials.

Lenses comprising previously known resins have a higher-refractive index than the lenses containing DAC, however, the refractive index thereof is still insufficient. Such resins have drawbacks such as high dispersion, poor weatherability and great specific gravity, since the resins are made from compounds containing numerous halogen atoms or aromatic rings to improve the refractive index.

It has been known to add an internal releasing agent during the process for preparing such lenses to improve mold release characteristics. In such process butyl phosphate is added to DAC. However, the addition of butyl phosphate is not required, and results in impaired appearance of the molded articles. [Seiichi Mima, "Polymer Digest", 3, 39 (1984) and the like].

In molding polyurethane and S-alkyl thiocarbamic acid ester lenses, it is difficult to release the lens from the mold after polymerization. In order to solve this problem, the present inventors invented a method in which an external releasing agent is employed (Japanese Patent Laid-open Publication No. 267316/1987) and a method in which a mold made from polyolefin resin is employed (Japanese Patent Laid-open Publication No. 236818/1987). In EP-A-0 271 839 (which is prior art under Art. 54 (3) EPC), the present applicant discloses lens resins formed from polyisocyanates that do not contain sulphur, and polythiols, with surface active agents as mould release agents.

However, these above mold release methods are still insufficient for improving mold release property in the cast polymerization because of the lens according to the present invention.

In the method in which an external releasing agent is employed, a surface treatment material for treating the inner surface of the mold is partially transferred to the surface and interior of the polymerized lenses, causing the lens surface to be uneven and turbid. The mold release treatment is required each time the mold is used. Accordingly, this method is intricate, decreases lens productivity, and thus is uneconomical.

Further, a polyolefin resin mold, is deformed at elevated temperatures, resulting in poor accuracy of the lens surfaces. Thus, the method cannot be applied in applications where high surface accuracy is required.

Preferred embodiments of the present invention may achieve one or more of the following:
 ameliorate the problems and disadvantages of the prior art by providing a lens having superior properties over prior art lenses, and a process for producing the lens;
 provide a lens having excellent optical properties;
 provide a colorless and transparent lens having a high refractive index;
 provide a process for producing lenses efficiently and economically on an industrial scale;
 provide plastic lenses having a high refractive index, high surface accuracy, excellent optical properties, excellent impact resistance, and which are lightweight and suitable for use in eyeglasses and cameras.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations, particularly pointed out in the appended claims.

5 JP-A-62 267 316 discloses lens resins derived from aromatic polyisocyanates which may contain sulphur, and polythiols.

The invention provides a process for producing a lens comprising reacting (a) one or more aliphatic polyisocyanate compounds having at least one sulfur atom with (b) one or more active hydrogen compounds selected from polyol compounds, polythiol compounds having sulfur atoms only in mercapto groups, and polythiol compounds having at least one sulfur atom in addition to the sulfur atom(s) contained in the mercapto group(s).

10 The present invention also provides a process for producing a lens containing the resin of the invention comprising forming a mixture of (a) one or more aliphatic polyisocyanate compounds having at least one sulfur atom; (b) one or more active hydrogen compounds selected from polyol compounds, polythiol compounds having sulfur atoms only in mercapto groups, and polythiol compounds having at least one sulfur atom in addition to the sulfur atom in the mercapto group(s) and (c) at least one internal releasing agent; pouring the mixture into a mold and polymerizing the mixture to form said lens.

15 A resin embodying the invention may have excellent optical properties, be colorless and of high refractive index. The plastic lenses of the invention may have high surface accuracy, excellent weatherability, exhibit excellent impact resistance and optical properties and be manufacturable extremely efficiently on an industrial scale by the use of a usual glass mold without any specific mold release treatment.

20 Reference will now be made in detail to the present preferred embodiments of the invention.

25 Exemplary aliphatic polyisocyanate compounds containing at least one sulfur atom and suitable for use in the processes of the invention include noncyclic aliphatic polyisocyanate compounds containing sulfur atom such as thiodiethyl diisocyanate, thiadipropyl diisocyanate, thiadihexyl diisocyanate, dimethylsulfine diisocyanate, dithiodimethyl diisocyanate, dithiodiethyl diisocyanate and dithiodipropyl diisocyanate; an aliphatic isocyanate containing sulfur atom and an aromatic ring such as bis[(4-isocyanatomethyl)benzene] sulfide; a cyclic aliphatic isocyanate containing sulfur atom such as 1,4-dithian-2,5-diisocyanate; and an aliphatic isocyanate containing sulfur atom and a heterocyclic ring.

30 Halogen-substituted compounds such as chlorine-substituted and bromine-substituted compounds of these polyisocyanates, biuret reaction products thereof, adduct reaction products of the polyisocyanates and trimethylol-propane, and dimerization and trimerization reaction products of the polyisocyanate compounds are also suitable for use in the process of the invention.

35 The polyisocyanate compounds may be used alone or in a mixture of two or more thereof.

Exemplary active hydrogen compounds suitable for use in the process of the invention include a polyol compound, a polythiol compound containing sulfur atoms only in mercapto groups, and a polythiol compound containing at least one sulfur atom in addition to the sulfur atom in mercapto groups.

40 Exemplary suitable polyol compounds include polyols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, neopentyl glycol, glycerin, trimethylolethane, trimethylolpropane, butanetriol, 1,2-methyl glycoside, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, erythritol, threitol, ribitol, arabinitol, xylitol, allitol, mannitol, dorcitol, iditol, glycol, inositol, hexanetriol, triglycerol, diglycerol, triethylene glycol, polyethylene glycol, tris(2-hydroxyethyl) isocyanurate, cyclobutanediol, cyclopantanediol, cyclohexanediol, cycloheptanediol, cyclooctanediol, cyclohexanedimethanol, hydroxypropylcyclohexanol, tricyclo(5,2,1,0^{2,6})decane dimethanol, bicyclo(4,3,0)nonanediol, 45 dicyclohexanediol, tricyclo(5,3,1,1)dodecanediol, bicyclo(4,3,0)nonanedimethanol, tricyclo(5,3,1,1)dodecane diethanol, hydroxypropyltricyclo(5,3,1,1)dodecanol, spiro(3,4)octanediol, butyl cyclohexanediol, 1,1-bicyclohexylidenediol, cyclohexanetriol, maltitol, lactitol, dihydroxynaphthalene, trihydroxynaphthalene, tetrahydroxynaphthalene, dihydroxybenzene, benzenetriol, biphenyltetraol, pyrogallol, (hydroxynaphthyl)-pyrogallol, trihydroxyphenanthrene, bisphenol A, bisphenol F, xylylene glycol, di(2-hydroxyethoxy)benzene, 50 bisphenol A-bis-(2-hydroxyethyl ether), tetrabromobisphenol A, tetrabromobisphenol A-bis(2-hydroxy ethyl ether), dibromoneopentyl glycol and epoxy resin; condensation reaction products of these polyols and organic polybasic acids such as oxalic acid, glutamic acid, adipic acid, acetic acid, propionic acid, cyclohexanecarboxylic acid, β -oxocyclohexanepropionic acid, dimer acid, phthalic acid, isophthalic acid, salicylic acid, 3-bromopropionic acid, 2-bromoglycolic acid, dicarboxycyclohexane, pyromellitic acid, 55 butanetetracarboxylic acid and bromophthalic acid; addition reaction products of the above-mentioned polyols and alkylene oxides such as ethylene oxide and propylene oxide; and addition reaction products of alkylene polyamines and alkylene oxides such as ethylene oxide and propylene oxide.

Halogen-substituted compounds such as chlorine-substituted and bromine-substituted compounds of these above polyol compounds are also suitable for use in the process of the invention.

45 Exemplary polythiol compounds containing at least one sulfur atom in addition to the sulfur atom in mercapto groups include aromatic polythiols such as 1,2-bis(mercaptomethylthio)benzene, 1,3-bis(mercaptomethylthio)benzene, 1,4-bis(mercaptomethylthio)benzene, 1,2-bis(mercaptoethylthio)benzene, 1,3-bis(mercaptoethylthio)benzene, 1,4-bis(mercaptoethylthio)benzene, 1,2,3-tris(mercaptomethylthio)-benzene, 1,2,4-tris(mercaptomethylthio)benzene, 1,3,5-tris(mercaptomethylthio)benzene, 1,2,3-tris(mercaptoethylthio)-benzene, 1,2,4-tris(mercaptomethylthio)benzene, 1,3,5-tris(mercaptoethylthio)benzene, 1,2,3,4-tetrakis(mercaptomethylthio)benzene, 1,2,3,5-tetrakis(mercaptomethylthio)benzene, 1,2,4,5-tetrakis(mercaptomethylthio)benzene, 1,2,3,4-tetrakis(mercaptomethylthio)benzene, 1,2,3,5-tetrakis(mercaptomethylthio)benzene, 1,2,4,5-tetrakis(mercaptomethylthio)-benzene and their nucleus-alkylated compounds; aliphatic polythiols such as bis(mercaptomethyl) sulfide, bis(mercaptoethyl) sulfide, bis(3-mercaptopropyl) sulfide, bis(mercaptomethylthio)methane, bis(2-mercaptoethylthio)methane, bis(3-mercaptopropylthio)methane, 1,2-bis(mercaptomethylthio)ethane, 1,2-bis(mercaptoethylthio)ethane, 1,2-bis(3-mercaptopropylthio)ethane, 1,3-bis(mercaptomethylthio)-propane, 1,3-bis(2-mercaptoethylthio)propane, 1,3-bis(3-mercaptopropylthio)propane, 1,2,3-tris(mercaptomethylthio)-propane, 1,2,3-tris(2-mercaptoethylthio)-

propane, 1,2,3-tris(3-mercaptopropylthio)propane, tetrakis(mercaptopropylthiomethyl)methane, tetrakis(2-mercaptopropylthiomethyl)-methane, tetrakis(3-mercaptopropylthiomethyl)methane, bis(2,3-dimercaptopropyl)sulfide, 2,5-dimercapto-1,4-dithiane, bis(mercaptopropyl) disulfide, bis(mercaptopropyl) disulfide, bis(mercaptopropyl) disulfide, and esters of these compounds and thioglycolic acid or mercaptopropionic acid, 5 hydroxymethyl sulfide bis(2-mercaptopropyl acetate), hydroxymethyl sulfide bis(3-mercaptopropionate), hydroxyethyl sulfide bis(2-mercaptopropyl acetate), hydroxyethyl sulfide bis(3-mercaptopropionate), hydroxypropyl sulfide bis(2-mercaptopropyl acetate), hydroxypropyl sulfide bis(3-mercaptopropionate), hydroxymethyl disulfide bis(2-mercaptopropyl acetate), hydroxymethyl disulfide bis(3-mercaptopropionate), hydroxyethyl disulfide bis(2-mercaptopropyl acetate), hydroxyethyl disulfide bis(3-mercaptopropionate), hydroxypropyl disulfide bis(2-mercaptopropyl acetate), hydroxypropyl disulfide bis(3-mercaptopropionate), 10 2-mercaptopropyl ethyl ether bis(2-mercaptopropionate), 2-mercaptopropyl ethyl ether bis(3-mercaptopropionate), 1,4-dithian-2,5-diobis(2-mercaptopropionate), thiodiglycolic acid bis(2-mercaptopropyl ester), thiodiglycolic acid bis(2-mercaptopropyl ester), thiodiglycolic acid bis(2-mercaptopropyl ester), 4,4-thiodibutylic acid bis(2-mercaptopropyl ester), dithiodiglycolic acid bis(2-mercaptopropyl ester), 4,4-dithiodibutylic acid bis(2-mercaptopropyl ester), thiodiglycolic acid bis(2,3-dimercaptopropyl ester), thiodiglycolic acid bis(2,3-dimercaptopropyl ester), dithioglycolic acid bis(2,3-dimercaptopropyl ester) and dithiopropionic acid bis(2,3-dimercaptopropyl ester); and heterocyclic compounds such as 3,4-thiophenedithiol, bismuthiol and 2,5-dimercapto-1,3,4-thiadiazole.

20 Halogen-substituted compounds such as chlorine-substituted and bromine-substituted compounds of the above polythiol compounds may also be employed. These active hydrogen compounds may be used alone or in a mixture of two or more thereof.

The molar ratio of the functional groups of the polyisocyanate compound to the functional groups of the active hydrogen compound is from about 0.5 to about 3.0, preferably from about 0.5 to about 1.5, i.e., NCO/(OH + SH).

25 In the plastic lens of the present invention, a urethane resin or an S-alkyl thiocarbamic acid ester resin is used as a raw material. Therefore in the plastic lens a urethane bond is present between an isocyanate group and a hydroxyl group, or an S-alkyl thiocarbamic acid ester bond is present between the isocyanate group and the mercapto group. However, the plastic lens of the present case may contain an allophanate bond, a urea bond, a biuret bond or the like in addition to the above bond depending on the intended end 30 use of the lens.

For example, the isocyanate group may be further reacted with the urethane bond or S-alkyl thiocarbamic acid ester bond so as to increase the crosslink density. In this case, the reaction temperature is set to 100°C or more, and the isocyanate component is used in an excess amount. Alternatively, an amine may be used to utilize the urea bond or biuret bond. When the isocyanate compound is reacted with 35 a compound other than the hydroxyl compound or mercapto compound, attention must be paid to coloring.

Various additives may be added to the raw materials to achieve particular properties for end use and lens of the invention. Exemplary suitable additives include a chain extender, a crosslinking agent, a light stabilizer, an ultraviolet absorbent, an anti-oxidant, an oil-soluble dye and a filler.

40 For the purpose of adjusting the reaction rate to a desired level, a known reaction catalyst may be added which can be generally used in the manufacture of the polyurethane or S-alkyl thiocarbamic acid ester.

The plastic lens of the present invention can be prepared by cast polymerization. One or more of aliphatic polyisocyanate compounds containing sulfur atom; one or more of active hydrogen compounds and at least one internal releasing agent are mixed to form a mixture; the resulting mixture is casted into a 45 mold, and then polymerization is carried out.

Exemplary suitable internal releasing agents useful in the present invention include fluorine containing nonionic surface active agents, silicon containing nonionic surface active agents, alkyl quaternary ammonium salts, acidic phosphates, liquid paraffins, waxes, higher fatty acids and metallic salts thereof, higher fatty esters, higher fatty alcohols, bisamides, polysiloxanes and aliphatic amine ethylene oxide adducts. 50 They can be suitably selected in view of the combination of monomers, polymerization conditions, economy and ease of handling.

The internal releasing agents may be used alone or in a mixture of two or more thereof.

The fluorine containing nonionic surface active agents and the silicon containing nonionic surface active agents, which are used as the internal releasing agents in the present invention, are compounds each 55 having a perfluoroalkyl group or a dimethylpolysiloxane group, a hydroxyalkyl group and a phosphoric ester group. Exemplary suitable fluorine containing nonionic surface active agents commercially available include Unidain™: DS-401 and DS-403 (products of Daikin Kogyo Co., Ltd.), F-Top™: EF122A, EF126 and EF301 (products of Shinakita Chemical Co., Ltd.). An exemplary silicon containing nonionic surface active agents is

a trial product Q2-120A of Dow Chemical Co..

Exemplary suitable alkyl quaternary ammonium salts useful as the internal releasing agents in the present invention include as cationic surface active agents such as alkyl quaternary ammonium salts including halogen salts, phosphates and sulfates of alkyl quaternary ammonium. Typical exemplary chlorides thereof include trimethylacetylammmonium chloride, trimethylstearylammmonium chloride, dimethylethylcetylammmonium chloride, triethylodecylammmonium chloride, trioctylmethylammnonium chloride and diethylcyclohexyldecylammnonium chloride.

Exemplary suitable acidic phosphate compounds for use as the internal releasing agent in the present invention include isopropyl acid phosphate, diisopropyl acid phosphate, butyl acid phosphate, dibutyl acid phosphate, octyl acid phosphate, dioctyl acid phosphate, isodecyl acid phosphate, diisodecyl acid phosphate, tridecanol acid phosphate and bis(tridecanol acid) phosphate.

Exemplary suitable metallic salts of the higher fatty acids useful as the internal releasing agents in the present invention include zinc salts, calcium salts, magnesium salts, nickel salts, copper salts and other salts of stearic acid, oleic acid, octanoic acid, lauric acid, behenic acid and ricinoleic acid such as zinc stearate, zinc oleate, zinc palmitate, zinc laurate, calcium stearate, calcium oleate, calcium palmitate, calcium laurate, magnesium stearate, magnesium oleate, magnesium laurate, magnesium palmitate, nickel stearate, nickel oleate, nickel palmitate, nickel laurate, copper stearate, copper oleate, copper laurate and copper palmitate.

Exemplary suitable higher fatty esters useful as the internal releasing agent in the present invention include esters of higher fatty acids such as stearic acid, oleic acid, octanoic acid, lauric acid and ricinoleic acid and alcohols such as ethylene glycol, dihydroxypropane, dihydroxybutane, neopentyl glycol and dihydroxyhexane.

The amount of the internal releasing agent to be used, which may be used alone or in the form of a mixture two or more thereof, is from about 0.1 to about 10,000 ppm, preferably from about 1 to about 5,000 ppm based on the total weight of a monomer mixture.

When the amount of the internal releasing agent is less than 0.1 ppm, mold release characteristics are bad; when it is in excess of 10,000 ppm, the lenses are turbid, and each lens is prematurely separated from the mold during polymerization and the surface accuracy of the lenses deteriorates.

Polymerization is carried out at from about -20°C to about 200°C, preferably from about room temperature to about 150°C, more preferably from about 50°C to about 120°C, in from 0.5 to 72 hours, depending upon the types of monomers and the mold releasing agent employed.

The polymerized lenses may be subjected to an annealing treatment, if necessary.

The plastic lenses of the present invention have high surface accuracy and excellent optical properties, are lightweight and excellent in impact resistance, and are suitable for optical element materials such as lenses of glasses and cameras.

Moreover, the plastic lenses of the present invention can be subjected to physical and chemical treatments such as surface abrasion treatment, antistatic treatment, hard coat treatment, non-reflective coat treatment, coloring treatment and dimming treatment for the prevention of reflection, enhancement of hardness, improvement of abrasion resistance and chemical resistance, prevention of turbidity, or to confer a fashionable appearance.

Now, the present invention will be further described and clarified by the following examples and comparative examples which are intended to be purely exemplary of the invention. The performance tests of the resins and lenses, specifically the tests of refractive index, Abbe's number, weatherability, mold release characteristics and appearance were carried out by the following procedure:

Refractive index and Abbe's number: Measured at 20°C by the use of a Pulflich refractometer.

Weatherability: A resin specimen was set on a weatherometer equipped with a sunshine carbon arc lamp, and after 200 hours had elapsed, the resin specimen was taken out therefrom. Afterward, the specimen was compared in tint with the resin for lens which had not been subjected to the test. Evaluation was made by the ranking of "not changed", "slightly yellowed" and "yellowed" denoted by "O", "Δ" and "X", respectively.

Mold release characteristics: When a polymerized lense was released from a mold without resistance, the mold release characteristics denoted by "O", and when a part or all of the lense was not released therefrom; they denoted by "X", by mean of driving in a Teflon wedge between the lens and the mold.

Appearance: It was evaluated by visual observation.

Example 1

18.4 g (0.09 mol) of dithiodiethyl diisocyanate were mixed with 8.0 g (0.06 mol) of 1,2,6-hexanetriol. The resulting mixture was poured into a mold composed of a glass mold and a gasket, the temperature was
5 raised slowly from room temperature to 120 °C taking 28 hours, to complete the polymerization. The thus obtained lens was colorless and excellent in weatherability, had a refractive index n_D^{20} of 1.57, an Abbe's number ν_D^{20} of 44 and a specific gravity of 1.32.

Examples 2 to 18 and Comparative Examples 1 to 3

10 Following the procedure of Example 1, lenses were prepared in composition ratios shown in Table 1. The results of performance tests are set forth in Table 1.

Example 19

15 18.4 g (0.09 mol) of dithioethyl diisocyanate, 8.0 g (0.06 mol) of 1,2,6-hexanetriol and 0.03 g of isopropyl acid phosphate were mixed. The resulting mixture was poured into a mold composed of a glass mold and a gasket, and was gradually heated from room temperature to 120 °C taking 28 hours, to complete the polymerization. After the polymerization, a lens was released from the mold with ease. The
20 thus obtained lens was colorless and had good surface accuracy. Moreover, it had a refractive index n_D^{20} of 1.57 and an Abbe's number ν_D^{20} of 44.

Examples 20 to 47

25 Following the procedure of Example 19, lenses were prepared in composition ratios shown in Table 2. The results of performance tests are set forth in Table 2.

Comparative Examples 4 to 27

30 Following the procedure of Example 19 with the exception that the undermentioned mold treatments were carried out, lenses were prepared in the composition ratios shown in Table 3. The results of performance tests are set forth in Table 3.

(1) No treatment.....A glass mold was used without any release treatment.

35 (2) External release treatment.....External mold releasing agent YSR-6209™ (product of Toshiba Silicon Co.) was applied and baked on the inner surface of a glass mold.

(3) Reuse of external release treatment.....The glass mold obtained by the external release treatment was once employed for the polymerization and then used again without any further treatment.

(4) Use of PP mold A polypropylene mold was prepared by injection molding and used in place of the glass mold without any surface treatment.

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Table 1 (I)

Active Hydrogen Compound	<u>Polyisocyanate</u>	Refrac- tive Index	Weather- ing Resist- ance		Appear- ance
			Abbe's Number	mol	
Example 2	Trimethylol- propane 0.06 mol	(SCH ₂ CH ₂ NCO) ₂ 0.09 mol	1.56	45	0 Trans- parent
Example 3	" 0.06 mol	S(CH ₂ CH ₂ NCO) ₂ 0.09 mol	1.55	46	0 "
Example 4	C(CH ₂ OCC ₂ SH) ₄ 0 0.04 mol	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.60	40	0 "
Example 5	" 0.04 mol	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	1.59	41	0 "
Example 6	C(CH ₂ OCC ₂ SH) ₄ 0 0.04 mol	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.61	39	0 "
Example 7	"	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	1.59	42	0 "
Example 8	C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.04 mol	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	1.66	36	0 "

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Table 1 (II)

	<u>Active Hydrogen Compound</u>	<u>Polyisocyanate</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>	<u>Weathering Resistance</u>	<u>Appearance</u>
Example 9	S(CH ₂ CH ₂ SH) ₂ 0.04 mol	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	1.65	35	0	Transparent
Example 10	"	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.66	34	0	"
Example 11	C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.04 mol	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.67	34	0	"
Example 12	Trimethylolpropane 0.04 mol	S(CH ₂ CH ₂ NCO) ₂ 0.10 mol	1.57	43	0	"
	C(CH ₂ OCC ₃ H ₇ CH ₂ SH) ₄ 0.02 mol					
Example 13	Ethylene glycol 0.02 mol	" 0.10 mol	1.62	37	0	"
	C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.04 mol					
Example 14	C(CH ₂ OCC ₃ H ₇ CH ₂ SH) ₄ 0.02 mol	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.64	35	0	"
	S(CH ₂ CH ₂ SH) ₂ 0.02 mol					

Table 1 (III)

			<u>Active Hydrogen Compound</u>	<u>Polyisocyanate</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>	<u>Weathering Resistance</u>	<u>Appearance</u>
Example 15	Trimethylolpropane 0.04 mol Diethylene glycol 0.02 mol			(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	1.57	45	0	Trans-parent
Example 16	C(CH ₂ OCC(O)CH ₂ SH) ₄ 0.02 mol C(CH ₂ OCC(O)CH ₂ SH) ₄ 0.02 mol			" 0.08 mol	1.61	40	0	"
Example 17	C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.02 mol S(CH ₂ CH ₂ SH) ₂ 0.02 mol			" 0.08 mol	1.66	35	0	"
Example 18	C(CH ₂ OCC(O)CH ₂ SH) ₄ 0.05 mol			S(CH ₂ CH ₂ NCO) ₂ 0.05 mol (SCH ₂ CH ₂ NCO) ₂ 0.05 mol	1.59	40	0	"

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Table 1 (IV)

	<u>Active Hydrogen Compound</u>	<u>Polyisocyanate</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>	<u>Weathering Resistance</u>	<u>Appearance</u>
Comp. Ex. 1	1,4-Butanediol 0.07 mol	1,6-Hexamethylene diisocyanate 0.07 mol	1.50	55	0	"
Comp. Ex. 2	1,2,3-Trimer-captobenzene 0.033 mol	" 0.05 mol	1.66	27	0	"
Comp. Ex. 3		1,3-Xylylene diisocyanate 0.05 mol	1.61	27	Δ	Slightly yellowed

Table 2 (I)

<u>Active Hydrogen Compound</u>	<u>Release Agent</u>	<u>Internal Release Characteristics</u>	<u>Release Appearance</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>
Polyiso-cyanate					
Dithio-dipropyl diiso-cyanate 0.09 mol	Trimethylol-propane 0.06 mol	Unidain DS-403 200 ppm	0	High surface accuracy, transparent	1.56 45
Example 20					
Exam- ple 21	Thiodiethyl diiso-cyanate 0.09 mol	" F-TOP EF-126 250 ppm	0	" 1.55	46
Exam- ple 22	"	" Q2-120A 500 ppm	0	" 1.55	46
Exam- ple 23	Dithio-diethyl diiso-cyanate 0.09 mol	Diethylene glycol 0.09 mol	0	" 1.57	45
Exam- ple 24	"	Trioctyl-methyl-ammonium chloride 500 ppm	"	" 1.58	44
		Isopropyl acid phosphate 500 ppm	0	"	

Table 2 (III)

	<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Internal</u> <u>Releas-</u> <u>ing Agent</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Exam- ple 25	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ OOCCH ₂ CH ₂ SH) ₄ 0.04 mol	Unidain DS-401 (Daikin) 100 ppm	0	High surface accuracy, Trans- parent	1.59	40
Exam- ple 26	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ OOCCH ₂ SH) ₄ 0.04 mol	Q-2-120A (Dow) 150 ppm	0	"	1.61	39
Exam- ple 27	"	"	Trimethyl- acetyl- ammonium chloride 500 ppm	0	"	"	"
Exam- ple 28	"	"	Diiso- propyl acid phosphate 500 ppm	0	"	"	"
Exam- ple 29	S(CH ₂ CH ₂ CH ₂ NCO) ₂ 0.08 mol	"	Unidain DS-403 (Daikin) 100 ppm	0	"	1.59	42

Table 2 (III)

	<u>Active Hydrogen Compound</u>	<u>Internal Releasing Agent</u>	<u>Release Characteristics</u>	<u>Appearance</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>
Polyiso-cyanate						
Example 30	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ OCH ₂ SH) 4 O 0.04 mol	Unidain DS-401 (Daikin). 100 ppm Q2-120A (Dow) 100 ppm	0 High surface accuracy, Transparent	1.59 42	
Example 31	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ OCH ₂ CH ₂ SH) 4 O 0.04 mol	Dibutyl acid phosphate 500 ppm	0 "	1.59 39	
Example 32	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	"	Trimethyl- octyl- ammonium chloride 500 ppm	0 "	1.58 41	
Example 33	"	C(CH ₂ SCH ₂ CH ₂ SH) 4 O 0.04 mol	Unidain DS-401 (Daikin) 100 ppm	0 "	1.66 36	

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Table 2 (IV)

<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Internal</u> <u>Releas-</u> <u>ing Agent</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Exam- ple 34	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.04 mol	Q2-120A (Dow) 150 ppm	0	High surface accuracy, Trans- parent	1.66 36
Exam- ple 35	"	"	Trimethyl- acetyl- ammonium chloride 500 ppm	"	"	"
Exam- ple 36	"	"	Diisopropyl acid phosphate 500 ppm	"	"	"
Exam- ple 37	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	"	Unidain DS-403 (Daikin) 100 ppm	0	" 1.67	34

Table 2 (V)

<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Internal</u> <u>Releas-</u> <u>ing Agent</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Exam- ple 38 0.08 mol	(SCH ₂ CH ₂ NCO) ₂ 0.04 mol	C(CH ₂ SCH ₂ CH ₂ SH) 4 0.04 mol	Unidain DS-401 (Daikin) 100 ppm Q2-120A (Dow) 100 ppm	0	High surface accuracy, Trans- parent	1.67 34
Exam- ple 39 0.08 mol	" 0.04 mol	S(CH ₂ CH ₂ SH) 2 0.04 mol	Dibutyl acid phosphate 500 ppm	0	" 1.66	" 34
Exam- ple 40 0.08 mol	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	"	Trimethyl- octyl- ammonium chloride 500 ppm	0	" 1.65	35
Exam- ple 41 0.10 mol	" 0.04 mol	Trimethylol propane C(CH ₂ OOCCH ₂ CH ₂ SH) 4 0.02 mol	Unidain DS-403 200 ppm	0	" 1.57	43

Table 2 (VI)

	<u>Active Hydrogen Compound</u>	<u>Internal Releasing Agent</u>	<u>Release Characteristics</u>	<u>Appearance</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>
Example 42	S(CH ₂ CH ₂ NCO) ₂ 0.10 mol	Ethylene glycol 0.02 mol C(CH ₂ SCH ₂ CH ₂ SH) ₄ 0.04 mol	Dibutyl acid phosphate 500 ppm	O	High surface accuracy, transparent	1.62 37
Example 43	(SCH ₂ ClLi ₂ NCO) ₂ 0.08 mol	C(CH ₂ OCC(=O)CH ₂ CH ₂ SH) ₄ 0.02 mol S(CH ₂ CHCH ₂ SH) ₂ 0.02 mol	Trimethyl octyl ammonium chloride 500 ppm	O.	"	1.64 35
Example 44	"	Trimethylol propane 0.04 mol Diethylene glycol 0.02 mol	Q2-120A (Dow) 500 ppm	O	"	1.57 45

Table 2 (VII)

<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Internal</u> <u>Releas-</u> <u>ing Agent</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Exam- ple 45	(SCH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ OOCCH ₂ CH ₂ SH) ₄ 0 0.02 mol C(CH ₂ OOCCH ₂ SH) ₄ 0 0.02 mol	Diisopropyl acid phosphate 500 ppm	0 " " " "	High surface accuracy, Trans- parent	1.61 40
Exam- ple 46	"	"	0	"	1.66	35
Exam- ple 47	S(CH ₂ CH ₂ NCO) ₂ 0.05 mol (SCH ₂ CH ₂ NCO) ₂ 0.05 mol	C(CH ₂ OOCCH ₂ CH ₂ SH) ₄ 0 0.05 mol	"	"	1.59	40

Table 3 (I)

	<u>Active Hydrogen Compound</u>	<u>Mold Treatment</u>	<u>Release Characteristics</u>	<u>Appearance</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>
Polyiso-cyanate	(SCH ₂ CH ₂ NCO) ₂	1,2,6-Hexanetriol 0.06 mol	No treatment	X	-	-
Comp. Ex. 4	"	"	External release treatment	Uneven surface, Transparent	1.57	44
Comp. Ex. 5	"	"	Reuse of external release treatment (mold used in Comp. Ex. 5)	X	-	-
Comp. Ex. 6	"	"	Use of PP mold	O	Bad surface accuracy, Transparent	1.57
Comp. Ex. 7	"	"	"	O	Bad surface accuracy, Transparent	44

Table 3 (II)

<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Mold</u> <u>Treat-</u> <u>ment</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Comp. Ex. 8	S(CH ₂ CH ₂ NCO) ₂ 0.09 mol	Trimethylol propane 0.06 mol	No treat- ment	X	-	-
Comp. Ex. 9	"	"	External release treat- ment	O	Uneven surface, Trans- parent	1.55
Comp. Ex. 10	"	"	Reuse of external release treatment (mold used in Comp. Ex. 9)	X	-	-
Comp. Ex. 11	"	"	Use of PP mold	O	Bad surface accuracy, Trans- parent	1.55

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Table 3 (III)

<u>Polyisocyanate</u>	<u>Active Hydrogen Compound</u>	<u>Mold Treatment</u>	<u>Release Characteristics</u>	<u>Appearance</u>	<u>Refractive Index</u>	<u>Abbe's Number</u>
Comp. Ex. 12 0.08 mol	(SCH ₂ CH ₂ NCO) ₂	C(CH ₂ OCCCH ₂ SH) 4 0.04 mol	No treatment	X	-	-
Comp. Ex. 13	"	"	External release treatment	O	Uneven surface, transparent	1.61
Comp. Ex. 14	"	"	Reuse of external release treatment (mold used in Comp. Ex. 13)	X	-	-
Comp. Ex. 15	"	"	Use of PP mold	0	Bad surface accuracy, transparent	1.61

Table 3 (IV)

<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Mold</u> <u>Treat-</u> <u>ment</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Comp. Ex. 16	$S(CH_2CH_2NCO)_2$ 0.08 mol	$C(CH_2OC(O)CH_2SH)_4$ 0.04 mol	No treatment	X	-	-
Comp. Ex. 17	"	"	External release treatment	O	Uneven surface, transparent	1.59 42
Comp. Ex. 18	"	"	Reuse of external release treatment (mold used in Comp. Ex. 17)	X	-	-
Comp. Ex. 19	$(SCH_2NCO)_2$ 0.08 mol	$C(CH_2OC(O)CH_2CH_2SH)_4$ 0.04 mol	Use of PP mold	O	Bad surface accuracy, Transparent	1.60 40

Table 3 (V.)

Polyiso-cyanate	Active Hydrogen Compound	Mold Treatment	Release Characteristics	Appearance	Refractive Index	Abbe's Number
Comp. Ex. 20 0.08 mol	(SCH ₂ CH ₂ NCO) ₂ 0.04 mol	C(CH ₂ SCH ₂ CH ₂ SH) 4 0.04 mol	No treatment	X	-	-
Comp. Ex. 21	"	"	External release treatment	O	Uneven surface, Transparent	1.66 36
Comp. Ex. 22	"	"	Reuse of external release treatment (mold used in Comp. Ex. 21)	X	-	-
Comp. Ex. 23	"	"	Use of PP mold	O	Bad surface accuracy, Transparent	1.66 36

Table 3 (VI)

	<u>Polyiso-</u> <u>cyanate</u>	<u>Active</u> <u>Hydrogen</u> <u>Compound</u>	<u>Mold</u> <u>Treat-</u> <u>ment</u>	<u>Release</u> <u>Charac-</u> <u>teristics</u>	<u>Appear-</u> <u>ance</u>	<u>Refrac-</u> <u>tive</u> <u>Index</u>	<u>Abbe's</u> <u>Number</u>
Comp. Ex. 24	S(CH ₂ CH ₂ NCO) ₂ 0.08 mol	C(CH ₂ SCH ₂ CH ₂ SH)4 0.04 mol	No treat- ment	X	-	-	-
Comp. Ex. 25	"	"	External release treat- ment	O	Uneven surface, Trans- parent	1.67	34
Comp. Ex. 26	"	"	Reuse of external release treatment (mold used in Comp. Ex. 25)	X	-	-	-
Comp. Ex. 27	S(CH ₂ CHCH ₂ SH) ₂ 0.04 mol	Use of PP mold	O	Bad surface accuracy, Trans- parent	1.66	34	

Claims

1. A plastic lens comprising the product of reacting one or more sulfur-containing aliphatic polyisocyanate compounds with one or more active hydrogen compounds selected from polyol compounds and polythiol compounds, wherein the proportion of the sulfur-containing aliphatic polyisocyanate compound

to the active hydrogen compound is a mole ratio of from 0.5 to 3.0 moles of functional isocyanate group per mole of functional (SH + OH) group.

2. The plastic lens of claim 1 wherein the polythiol compounds are polythiol compounds having at least
5 one sulfur atom in addition to the mercapto groups.
3. A process for producing the plastic lens of claim 1 or claim 2 comprising adding at least one internal
10 mold releasing agent to the mixture of one or more sulfurcontaining aliphatic polyisocyanate com-
pounds and one or more active hydrogen compounds followed by casting polymerization, wherein the
internal mold releasing agent is selected from fluorine containing nonionic surface active agents, silicon
containing nonionic surface active agents,, alkyl quaternary ammonium salts, and acidic phosphates;
wherein the internal mold releasing agent is present in an amount of from 0.1 to 10,000 ppm based on
the total parts of the sulfur-containing aliphatic polyisocyanate compound and the active hydrogen
compound; and wherein the casting polymerization is carried out in a temperature range from -20 °C to
15 200 °C.

Patentansprüche

1. Eine Kunststofflinse, umfassend das Produkt der Umsetzung von einer oder mehreren schwefelhaltigen
20 aliphatischen Polyisocyanatverbindungen mit einer oder mehreren aktiven Wasserstoff-Verbindungen,
die aus Polyolverbindungen und Polythiolverbindungen ausgewählt sind, wobei das Verhältnis der
schwefelhaltigen aliphatischen Polyisocyanatverbindung zu der aktiven Wasserstoff-Verbindung ein
Molverhältnis von 0,5 bis 3,0 Mol funktioneller Isocyanatgruppe pro Mol funktioneller (SH + OH)-Gruppe
ist.
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2. Die Kunststofflinse nach Anspruch 1, bei der die Polythiolverbindungen Polythiolverbindungen mit
wenigstens einem Schwefelatom zusätzlich zu den Mercaptogruppen sind.
3. Ein Verfahren zum Herstellen der Kunststofflinse nach Anspruch 1 oder Anspruch 2, umfassend, daß
30 wenigstens ein eingearbeitetes Formentrennmittel zu dem Gemisch aus einer oder mehreren schwefel-
haltigen aliphatischen Polyisocyanatverbindungen und einer oder mehreren aktiven Wasserstoff-Verbin-
dungen hinzugegeben wird, woraufhin Gießpolymerisation folgt, wobei das eingearbeitete Formentrenn-
mittel aus Fluor enthaltenden nicht-ionischen oberflächenaktiven Mitteln, Silizium enthaltenden nicht-
35 ionischen oberflächenaktiven Mitteln, Alkyl-quartären-ammoniumsalzen und sauren Phosphaten ausge-
wählt ist;
wobei das eingearbeitete Formentrennmittel in einer Menge von 0,1 bis 10.000 ppm, bezogen auf die
Gesamtheit der Teile der schwefelhaltigen aliphatischen Polyisocyanatverbindung und der aktiven
Wasserstoff-Verbindung, vorhanden ist; und wobei die Gießpolymerisation in einem Temperaturbereich
von -20 °C bis 200 °C durchgeführt wird.
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Revendications

1. Une lentille plastique comprenant le produit de la réaction d'un ou de plusieurs polyisocyanates
aliphatiques soufrés avec un ou plusieurs composés à hydrogène actif choisis parmi les polyols et les
45 polythiols, où la proportion du polyisocyanate aliphatique soufré au composé à hydrogène actif est un
rapport molaire de 0,5 à 3,0 moles de groupe fonctionnel isocyanate par mole de groupe fonctionnel
(SH + OH).
2. La lentille plastique de la revendication 1, dans laquelle les polythiols sont des polythiols ayant au
moins un atome de soufre en plus des groupes mercapto.
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3. Un procédé pour la production de la lentille plastique de la revendication 1 ou de la revendication 2,
comprenant l'addition d'au moins un agent de démolage interne au mélange d'un ou de plusieurs
polyisocyanates aliphatiques soufrés et d'un ou de plusieurs composés à hydrogène actif, puis la
polymérisation par coulée, où l'agent de démolage interne est choisi parmi les agents tensio-actifs
non ioniques fluorés, les agents tensio-actifs non ioniques siliciés, les sels d'alkylammonium quaternai-
re et les phosphates acides ; où l'agent de démolage interne est présent en une proportion de 0,1 à
55 10 000 ppm, relativement aux parties totales du polyisocyanate aliphatique soufré et du composé à

hydrogène actif ; et où la polymérisation par coulée est réalisée dans une gamme des températures de -20 °C à 200 °C.

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